



Speciation analysis of ^{129}I in seawater using coprecipitation and accelerator mass spectrometry and its applications

Xing, Shan; Hou, Xiaolin; Aldahan, Ala; Possnert, Göran

Published in:
Journal of Radioanalytical and Nuclear Chemistry

Link to article, DOI:
[10.1007/s10967-016-5060-6](https://doi.org/10.1007/s10967-016-5060-6)

Publication date:
2017

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Xing, S., Hou, X., Aldahan, A., & Possnert, G. (2017). Speciation analysis of ^{129}I in seawater using coprecipitation and accelerator mass spectrometry and its applications. *Journal of Radioanalytical and Nuclear Chemistry*, 311(1), 833–841. <https://doi.org/10.1007/s10967-016-5060-6>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Speciation analysis of ^{129}I and ^{127}I in Seawater using Co-precipitation and Accelerator Mass Spectrometry and Its Applications

Shan Xing¹ • Xiaolin Hou^{1,2,*}

¹ State Key Laboratory of Loess and Quaternary Geology, Shaanxi Key Laboratory of Accelerator Mass Spectrometry Technology and Application, Xi'an AMS Center, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an 710061, China

² Technical University of Denmark, Center for Nuclear Technologies, Risø Campus, Roskilde 4000, Denmark

Abstract

Speciation analysis of long-lived ^{129}I in seawater can provide useful information on the source of water masses. This paper presents an improved method for speciation analysis of ^{129}I based on coprecipitation of iodide as AgI with Ag_2SO_3 and AgCl. By adding small amount of ^{127}I carrier, the separation efficiency of iodine species and the accuracy and precision of ^{129}I measurement are remarkably improved. Depth profiles of ^{129}I species in seawater from the Antarctica were analyzed for investigation of the water circulation in the Antarctic, and the results are presented.

Keywords Iodine-129 • Chemical species • Accelerator mass spectrometry • Seawater

Introduction

Iodine exists predominantly as dissolved iodate, iodide, and a minute amount of organic iodine in the ocean [1]. Because of the strong biological activities, relatively high iodide concentration is often found in surface water, coastal and estuary areas [2, 3]. Therefore, the transformation of iodine species can reflect the change of marine

* Corresponding author: xiho@dtu.dk;

biological activity.

Due to low concentration of iodine in seawater, iodine carrier is normally added as carrier for separation of ^{129}I from matrix using solvent extraction [4, 5], this is not suitable for the determination of low level ^{129}I in the seawater received less anthropogenic ^{129}I such as those collected in southern hemisphere including the Antarctic and deep seas, because of contribution of ^{129}I in the iodine carrier to the sample during sample preparation. A rapid and simple coprecipitation method for separation of iodine (^{127}I and ^{129}I) species from seawater for measurement of $^{129}\text{I}/^{127}\text{I}$ using accelerator mass spectrometry (AMS) has been reported by our group [6]. Accelerator mass spectrometry (AMS) is the most suitable method for determination of ultralow level $^{129}\text{I}/^{127}\text{I}$ in natural samples with a $^{129}\text{I}/^{127}\text{I}$ atomic ratio $< 10^{-10}$ [2, 7-11], especially collected from the southern hemisphere and the deep seas, such as the Antarctic. However, due to low concentration of iodine in samples, ^{127}I signal in AMS measurement of the target prepared using carrier-free coprecipitation method is very weak, causing the measurements of both ^{127}I and ^{129}I unreliable. This work aims to improve the method of speciation analysis of ^{129}I by increasing the ^{127}I signal in AMS measurement. Meanwhile, species of ^{129}I and ^{127}I in seawater profiles from in the Antarctic are analyzed to demonstrate the application of speciation of ^{129}I in marine environmental tracer.

Materials and methods

Samples and chemicals

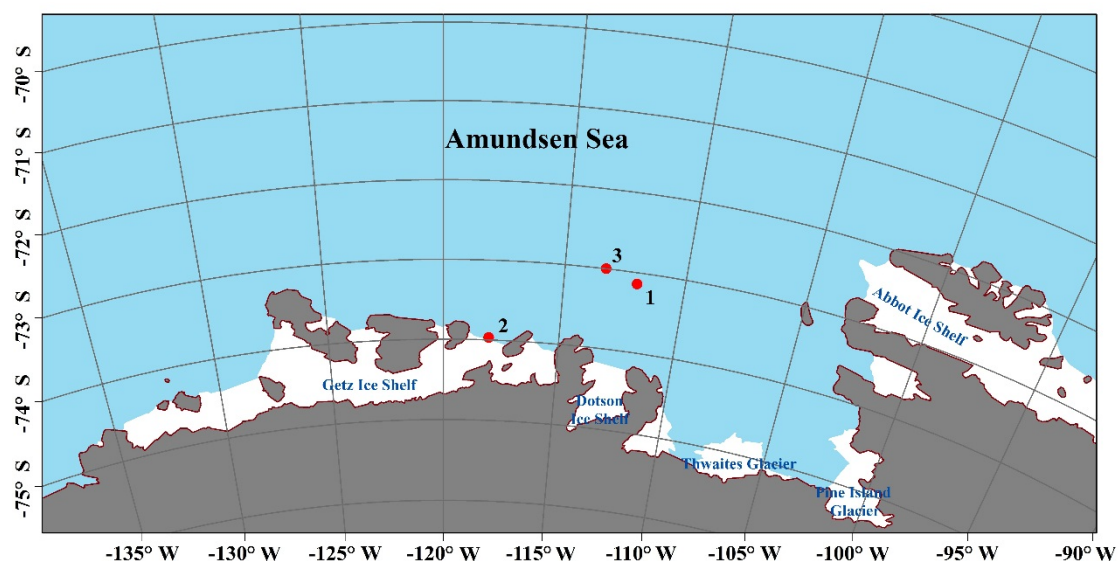


Fig. 1 Sampling locations (indicated as red dots) of seawater profiles in the Amundsen Sea, Antarctica

Seawater profiles from 3 sampling location were collected using a CTD rosette consisting of Niskins bottles and CTD sensors in the research vessel N.B. Palmer during cruise in the Amundsen Sea, Antarctica (73°-74° S, 111°-114° E) in December, 2010 (Fig. 1). Meanwhile, salinity, seawater temperature and concentrations of chlorophyll, phosphate, nitrite, total nitrogen, ammonium, silicate and partial pressure of CO₂ were measured by on-line detecting system of research vessel (Table 1). One seawater sample was collected in the open sea of the Yellow Sea (43°29.5'N, 121°59.1'E) in January, 2013. Certified reference material IAEA-418 was provided by International Atomic Energy Agency collected at the DY-FAMED station (43°25.117'N, 7°50.040'E) in the open Mediterranean Sea on 18 February, 2001.

¹²⁹I standard solution (NIST-SRM-4949c) was purchased from the National Institute Standard and Technology (Gaithersburg, MD). ¹²⁷I carrier solution with low ¹²⁹I level (¹²⁹I/¹²⁷I atomic ratio < 2×10⁻¹⁴) was prepared by dissolution of iodine crystal (Woodward iodine, Woodward Iodine Corporation, Oklahoma, U.S.A.) into 0.40 mol/L

NaOH-0.05 mol/L NaHSO₃ solution. ¹²⁷I⁻ carrier (KI, ¹²⁹I/¹²⁷I atomic ratio < (2.0±0.3)×10⁻¹³) was purchased from Shantou Xilong Chemical Factory in Shantou, China. All chemical reagents used were of analytical grade, and all solutions were prepared using deionized water (18.2 MΩ·cm).

Table 1 Salinity, seawater temperature and concentrations of chlorophyll, pCO₂, phosphate, nitrite, total nitrogen, ammonium and silicate observed in the Amundsen Sea, Antarctica

Sampling station	Depth(m)	Salinity (psu)	Seawater temperature (°C)	chlorophyll (µg/L)	pCO ₂ (µatm)	Phosphate (µM)	Nitrite (µM)	Total nitrogen(µM)	Ammonium (µM)	Silicate (µM)
1	2	33.8	-0.81	20.5	180.5	0.97	0.0284	13.9	0.121	80.7
	100	34.1	-1.63	—	—	1.93	0.0461	30	0.0576	89.3
	200	34.1	-1.72	—	—	1.97	—	30.6	—	83.4
	350	34.3	-1.11	—	—	2.16	—	33.6	—	102
	394	34.4	0.19	—	—	2.18	—	34.6	—	108
2	2	33.9	-1.45	1.41	382	1.85	0.0284	27.7	0.0871	93.1
	100	34.0	-1.70	—	—	1.89	0.0235	29.1	0.291	97.8
	260	34.1	-1.79	—	—	1.91	0.0306	29.7	0.217	101
	640	34.5	0.44	—	—	2.16	—	34.7	—	103
	750	34.5	0.62	—	—	2.13	—	34.4	—	102
	1227	34.6	-0.79	—	—	2.12	—	33	—	104

	2	33.8	0.12	26.2	193.9	1.07	0.0268	15.2	0.219	80.1
	100	34.1	-1.63	—	—	1.89	0.0496	30.6	0.0693	84.5
3	240	34.2	1.24	—	—	2.02	—	32.8	—	101
	350	34.3	-0.19	—	—	2.12	—	33.7	—	103
	422	34.6	0.56	—	—	2.15	—	34.2	—	111

Separation of iodine and its chemical species in seawater

After removal of potential suspended particles in the seawater by filtration through a 0.45 µm membrane, 0.60 L and 1.20 L of seawater were taken for separation of total iodine and iodine species respectively. 0.60 L seawater was transferred to a beaker. 0.5 kBq of $^{125}\text{IO}_3^-$ tracer was spiked, 0~1.0 mg of ^{127}I carrier and 0.50 ml of 2.0 mol/L NaHSO_3 solution were added into the beaker, and then 3.0 mol/L HNO_3 was added to adjust pH 1–2 to convert all iodine species to iodide. 30 mg Ag^+ (28 ml of 0.01 mol/L AgNO_3 solution) was dropwise added to the sample solution under stirring to form $\text{AgI-AgCl-Ag}_2\text{SO}_3\text{-AgBr}$ coprecipitate. The precipitate was separated by centrifuge and sequentially washed with 3.0 mol/L HNO_3 , H_2O , 30% and 20% NH_4OH to remove Ag_2SO_3 and most of AgCl and AgBr until 1-3 mg of precipitate was obtained. The detailed method for separation of iodine as AgI-AgCl precipitation from seawater has been reported elsewhere [6].

1.20 L seawater was transferred to a beaker for separation of iodide in seawater. 0.5 kBq of $^{125}\text{I}^-$ tracer and 0~1.0 mg of $^{127}\text{I}^-$ carrier (KI , $^{129}\text{I}/^{127}\text{I}$ atomic ratio $< 2.0 \times 10^{-13}$ carrier) were spiked, NaHSO_3 was added into the sample to a final concentration of 0.30 mmol/L, and then 0.5 mol/L HNO_3 was slowly added under stirring to adjust pH 4.2-5.5 (measured using a pH meter). 150 mg Ag^+ (45 ml of 0.03 mol/L AgNO_3) was dropwise added to the solution to form $\text{AgI-AgCl-Ag}_2\text{SO}_3\text{-AgBr}$ coprecipitate. The precipitate was separated by centrifuge and the supernatant was used for separation of iodate. The separated precipitate was sequentially washed with 3.0 mol/L HNO_3 , H_2O , 30% and 20% NH_4OH until 1-3mg of precipitate were obtained. To the supernatant, 0.5 kBq $^{125}\text{IO}_3^-$ tracer was spiked, 0.1-0.2 mg of ^{127}I carrier, 0.5 ml of 2.0 mol/L NaHSO_3 solution were added, and then 3.0 mol/L HNO_3 was added to adjust pH 1–2 to convert all iodine species to iodide. The following procedure was the same as that for total

iodine. The detailed AgI–AgCl precipitation method has also been reported elsewhere [6]. The diagram of the analytical procedure is schematically shown in Fig. 2.

^{125}I in the precipitate was measured using a NaI gamma detector (Model FJ-2021, Xi'an Nuclear Instrument factory, Xi'an, China) for monitoring the chemical yield of iodine in the procedure. The recovery of iodine species in the entire procedure is higher than 80%.

As in our previous work [12], two ^{129}I standard solutions, with a total iodine concentration of 1.00 mg/ml and $^{129}\text{I}/^{127}\text{I}$ atomic ratios of 9.954×10^{-12} and 1.138×10^{-10} respectively, were first prepared by dilution of ^{129}I standard solution (NIST-SRM-4949c) with ^{127}I carrier solution. Two ^{129}I working solutions were prepared by mixing the above prepared ^{129}I standard solution with NaCl solution in Cl/I mass ratio of 2:1. From each standard, 1.0 ml of working solution was taken to a 15 ml centrifuge tube, after addition of 0.5 kBq of $^{125}\text{I}^-$ tracer, 0.10 ml of 2.0 mol/L NaHSO_3 , 0.20 mL of 3.0 mol/L HNO_3 , and 2.0 ml of 1.0 mg/ml Cl^- were added. after mixed, 0.20 ml of 1.0 mol/L AgNO_3 was added to coprecipitate iodine as AgI–AgCl After centrifuge, the precipitate was sequentially washed with 3.0 mol/L HNO_3 and deionized water. For ^{129}I standards in AgI form, the $^{129}\text{I}/^{127}\text{I}$ standard solution with a total iodine concentration of 1.0 mg/ml was first converted to iodide by NaHSO_3 in acidic medium, and then AgNO_3 was added to directly precipitate iodide as AgI.

The procedure blank samples were prepared using the same procedure as for separation of total iodine, iodide and iodate in seawater but no sample was added. The prepared AgI–AgCl or AgI precipitate was analyzed for ^{129}I using AMS.

Iodine in the commercial ^{125}I tracer exists as iodide (NaI). To synthesize $^{125}\text{IO}_3^-$ tracer, $^{125}\text{I}^-$ solution was taken to a beaker, NaClO was added, then HCl is added to adjust pH 1-2 to oxidize iodide to iodate. The remained NaClO in the solution was

decomposed by heating at 80°C. The residue is dissolved in water and passed through a small anion exchange column (AG 1-×4 resin, NO₃⁻ form, 1.0 cm in diameter and 5 cm in height). The effluent containing iodate was collected and used as ¹²⁵IO₃⁻ tracer.

50 ml of seawater was taken to a beaker and ¹²⁵I⁻ was spiked. The sample was loaded to an anion exchange column (1.0 × 5.0 cm, AG1-×4 resin, NO₃⁻ form), the column is rinsed with 10 ml of 0.2 mol/L NaNO₃. The influent and rinse solution were collected and combined for ¹²⁷IO₃⁻ determination. Iodide on the column was eluted with 5% NaClO, and the eluate was used for determination of ¹²⁷I. ¹²⁵I in the iodide fraction was measured by gamma spectrometer to monitor chemical recovery of iodide during column separation.

AMS measurement of ¹²⁹I

The separated AgI–AgCl coprecipitate was dried in an oven at 60-70 °C for 3-6 h, the dried precipitate was ground to a fine powder and mixed with five times by mass of niobium powder (325-mesh, Alfa Aesar, Ward Hill, MA), which was finally pressed into a copper holder using a pneumatic press (Zhenjiang Aode Presser Instruments Ltd.). ¹²⁹I/¹²⁷I atomic ratios in the prepared targets were measured by AMS using 3MV Tandem AMS system (HVEE) in the Xi'an AMS center. I⁵⁺ ions were chosen for the measurement, where ¹²⁷I⁵⁺ was measured as charges (current) using a Faraday cup and ¹²⁹I⁵⁺ was measured using a gas ionization detector. All samples were measured for 6 cycles and 5 min per sample in each cycle. A detailed description of AMS system and measurement of ¹²⁹I has been reported elsewhere [13].

Measurement of ¹²⁷I concentration by ICP-MS

1.0 mL sample solution of the iodide fraction and the iodate fraction separated

using anion exchange column and the original seawater were taken to a vial, Cs^+ solution was spiked to a concentration of 2 ng/mL, and the samples were diluted for 10 times using 1% NH_4OH solution. ^{127}I in the prepared samples was measured using ICP-MS (X- series II, Thermo Scientific, USA). The detection limit of 0.02 ng/mL for ^{127}I was obtained. Iodide concentration was corrected for chemical yield during column separation.

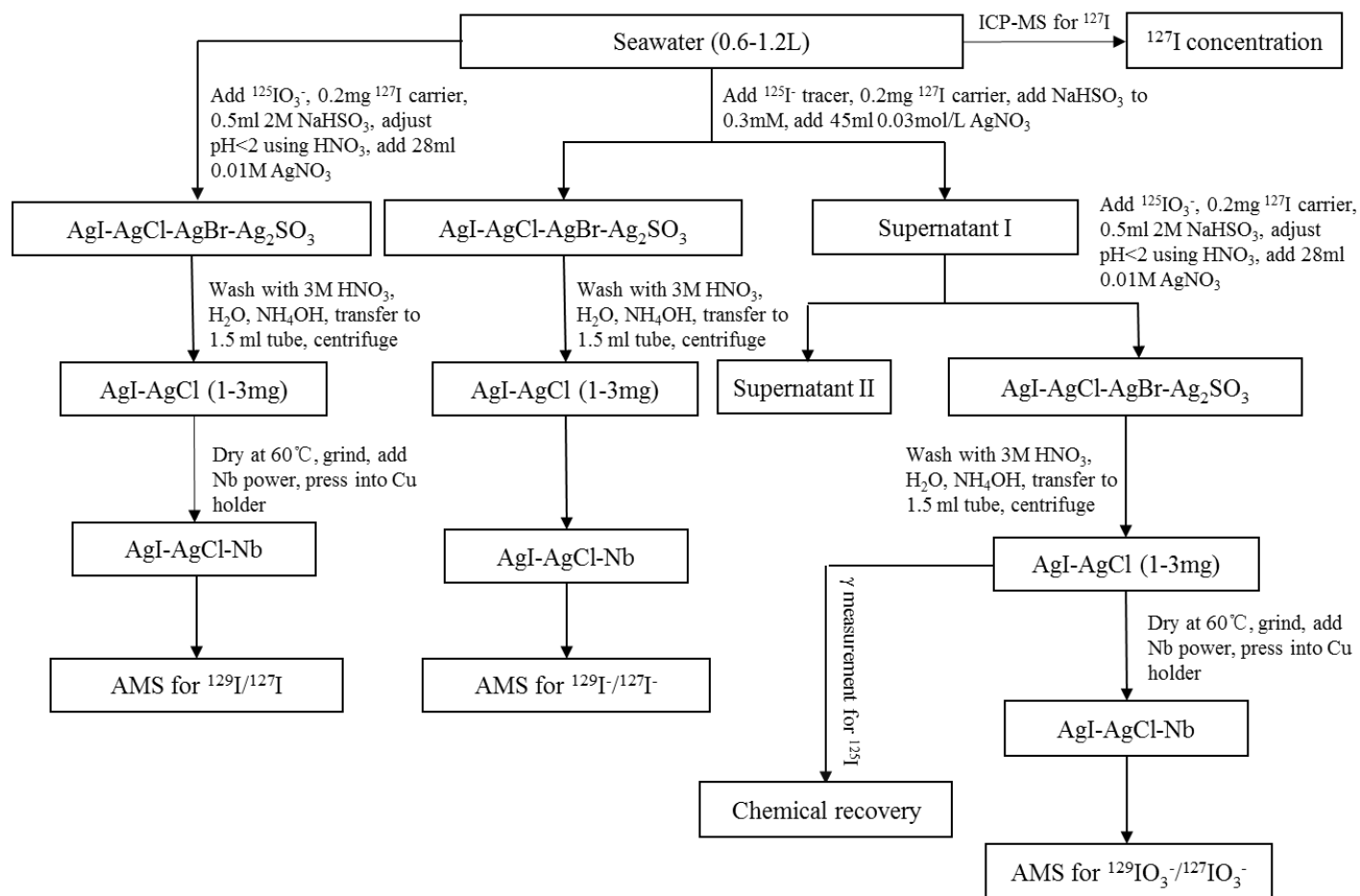


Fig. 2 Schematic diagram of the analytical procedure for speciation analysis of ^{129}I in seawater

Table 2 Results of ^{129}I and ^{127}I signals in background, blanks and standards, as well as in IAEA-418 ^d treated using solvent extraction and coprecipitation and measured by AMS in the AgI–AgCl targets

Sample	Intensity of signals in 5 min ^a		Measured ^{129}I concentration ($\times 10^8$ at/L)	Measured $^{129}\text{I}/^{127}\text{I}$ ratio ^b ($\times 10^{-11}$)
	$^{127}\text{I}^{5+}$, nA	$^{129}\text{I}^{5+}$, counts/min		
Background (Nb power)	0.27 \pm 0.12	0.2 \pm 0.1		
Procedure blank1	209.5 \pm 17.4	5.4 \pm 0.4		0.03 \pm 0.003
Procedure blank2	164.1 \pm 17.9	4.6 \pm 0.7		0.04 \pm 0.004
Standard -1 (AgI) ^c	590.7 \pm 1.9	5030 \pm 300		11.35 \pm 0.17
Standard-1 (AgI–AgCl) ^c	198.4 \pm 1.04	1697 \pm 198		11.41 \pm 0.18
Standard-2 (AgI–AgCl) ^c	264.64 \pm 6.0	202.4 \pm 23.0		1.02 \pm 0.03
IAEA-418 (solvent extraction)	511.6 \pm 4.2	794.4 \pm 96.0	2.52 \pm 0.044	96.3 \pm 1.69
IAEA-418 (coprecipitation)	470.1 \pm 3.1	1806 \pm 184	2.54 \pm 0.042	97.1 \pm 1.62

^a The results are given as average and 1 standard division of 6 measurements. ^b Average of six measurements, corrected by comparison with standard and blank subtraction. ^c The defined $^{129}\text{I}/^{127}\text{I}$ atomic ratio of 1.138×10^{-10} (standard-1) and 9.954×10^{-12} (standard-2) according to certified value in ^{129}I standard (NIST-SRM-4949c) and ^{127}I carrier prepared using iodine crystal (Woodward iodine). ^d The certified value of ^{129}I in the certified reference material IAEA-418 is $(2.16\text{--}2.73) \times 10^8$ atom/L [14].

Results and discussion

Influence of the amount of ^{127}I carrier on ^{129}I measurement

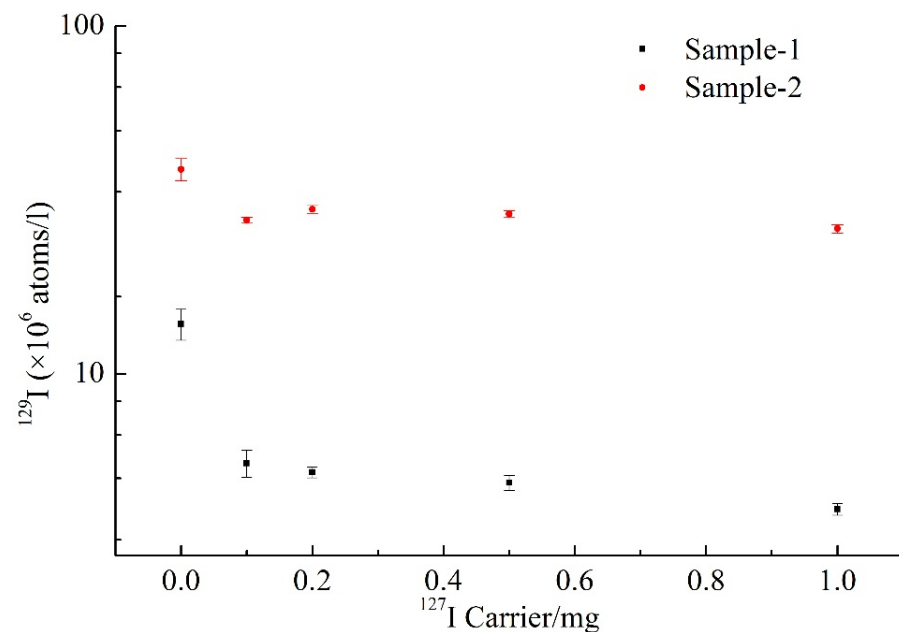


Fig. 3 Variation of the measured concentration of ^{129}I with the amount of ^{127}I carrier

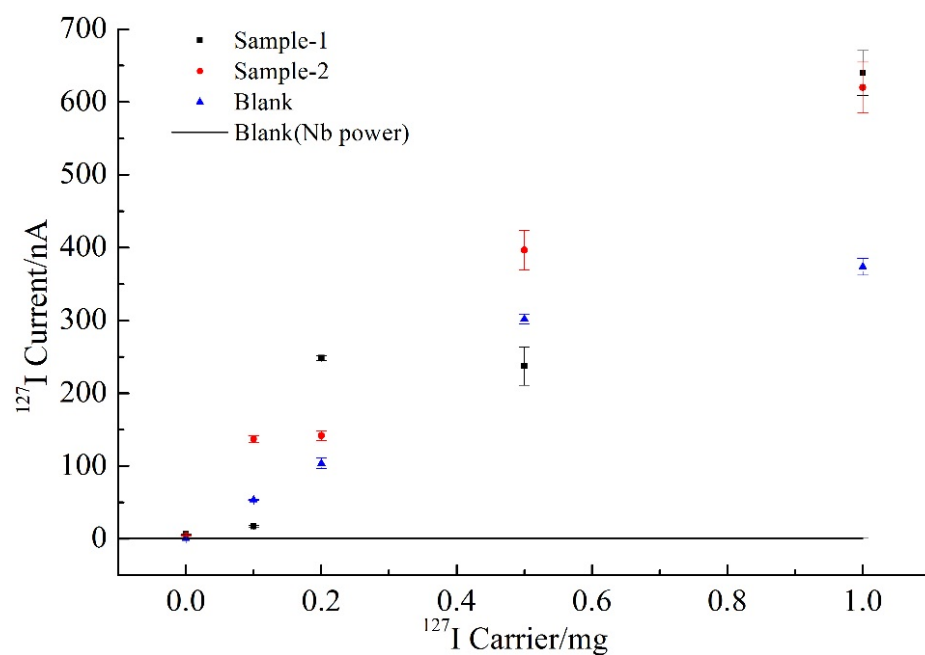


Fig. 4 Variation of the measured ^{127}I current with the amount of ^{127}I carrier

Fig. 3 shows the variation of measured concentration of ^{129}I with the amounts of added ^{127}I carrier in samples. The concentration of ^{129}I (13.9×10^6 atoms/L for sample-1

and 38.7×10^6 atoms/L for sample-2) by the carrier free AgI-AgCl coprecipitation method is 1.5-3.5 times higher than these measured by the carrier added AgI-AgCl coprecipitation method, which concentrations of ^{129}I measured range from 4.08×10^6 atoms/L to 5.53×10^6 atoms/L for sample-1 and 26.1×10^6 atoms/L to 29.7×10^6 atoms/L for sample-2. Fig. 4 shows the variation of the measured ^{127}I current with the amounts of added ^{127}I carrier in samples. The ^{127}I signal (137-620 nA) of sample-2 in the target by the carrier added AgI-AgCl coprecipitation method is two to three orders of magnitude higher than that (4.4 nA) by the carrier free AgI-AgCl coprecipitation method and that (0.77 nA) in the process blank. It is indicated that the low concentration of iodine in sample might produce a low ^{127}I signal in AMS measurement.

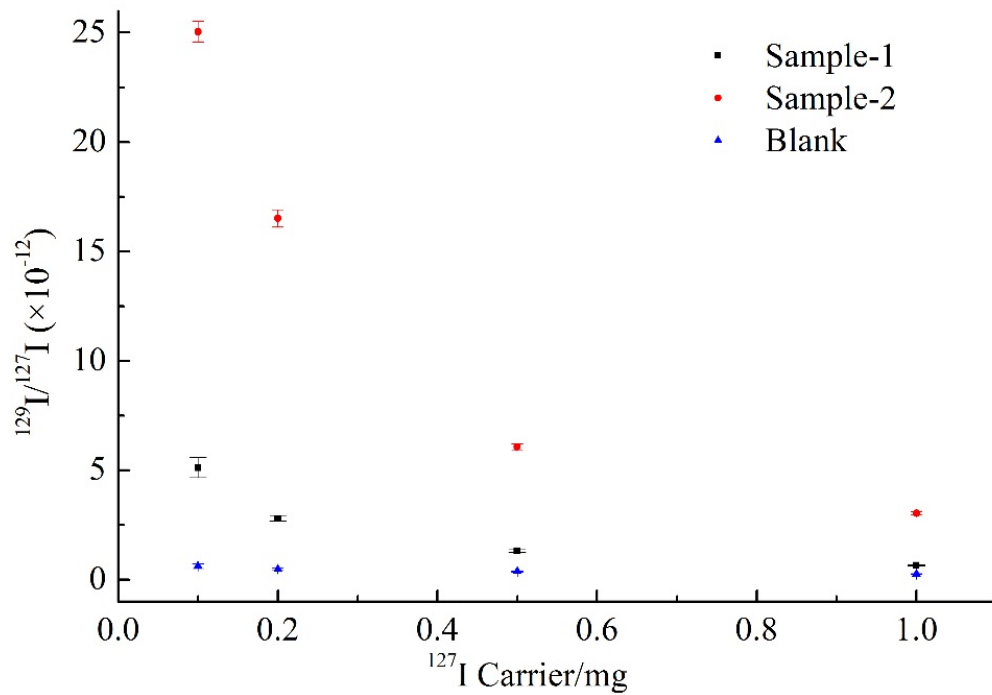


Fig. 5 Variation of the measured $^{129}\text{I}/^{127}\text{I}$ ratios with amount of ^{127}I carrier

The amount of ^{127}I carrier is a key parameter for improving the measurement accuracy and precision of ^{129}I . Fig. 5 shows variation of the measured $^{129}\text{I}/^{127}\text{I}$ ratios with the amount of added ^{127}I carrier in samples. The difference between the measured

$^{129}\text{I}/^{127}\text{I}$ ratios of sample and procedure blank decreases with the increase of ^{127}I carrier. When 1.0 mg ^{127}I carrier is added, the measured $^{129}\text{I}/^{127}\text{I}$ value of sample-1 with a $^{129}\text{I}/^{127}\text{I}$ atomic ratio $\sim 10^{-11}$ ($(0.65 \pm 0.02) \times 10^{-12}$) was close to that of the blank ($(0.26 \pm 0.02) \times 10^{-12}$), which increases the analytical uncertainty of ^{129}I in the sample after a correction for the blank. T-test of the results of $>0.5\text{mg}$ ^{127}I carrier shows no significant difference between the sample-1 and blank at $p > 0.05$. When the amount of ^{127}I carrier was reduced to 0.1-0.2 mg, the measured $^{129}\text{I}/^{127}\text{I}$ value in the sample-1 was one order of magnitude higher than that in blank. Furthermore, because of contribution of ^{129}I in the iodine carrier to the sample, addition of more amount of ^{127}I carrier is not suitable for the determination of low level ^{129}I in the seawater. These results reveal that addition of small amount of carrier (0.1-0.2 mg) in the sample can significantly arise the measurement uncertainty in AMS measurement, especially in the low level sample.

Reliability of the measurement of ^{129}I and its species in seawater

In this work, the chemical recovery of iodine in overall separation procedure measured using ^{125}I which was spiked into the sample in the beginning of the separation to be higher than 80%. It should be mentioned that a high recovery of iodine is crucial for accurate measurement of ^{129}I in low level samples, such as those collected from the Antarctic due to the very low concentration of ^{129}I . Meanwhile, the sensitive measurement, procedure blank, and background of instrument are also important for the measurement of low level ^{129}I . The procedure blanks for analysis of seawater samples were prepared using the same procedure as for the sample, the instrumental background was prepared by pressed only Nb powder into target holder, the measurement results including the measured signal intensity of ^{127}I and ^{129}I in these blanks, standards and IAEA-418 are presented in Table 2. The measured $^{129}\text{I}/^{127}\text{I}$ atomic

ratios in the procedure blanks are lower than 4×10^{-13} , which is two to three orders of magnitude higher than those in the standards and IAEA-418. This low blank level and the high sensitivity of AMS for ^{129}I measurement ensure the reliability of the analytical results of ^{129}I in these low-level samples. It can be observed that compared with the standards and IAEA-418, the ^{129}I signal (4.6-5.4 counts/min) in the procedure blanks of snow are slightly higher than that ((0.2 \pm 0.1) counts/min) in the instrumental background, indicating no significant contribution of ^{129}I signal from the chemical separation and target preparation procedure. ^{127}I signal in the procedure blank and IAEA-418 prepared by coprecipitation method using 200 μg ^{127}I carrier ((164.1-470.1) nA) is more than 30 times higher than that of instrument background (Nb powder, 0.27 nA) (Table 2), ensuring a reliable and stable ^{127}I signal in the AMS measurement. The measured $^{129}\text{I}/^{127}\text{I}$ ratios in two types of standards prepared by AgI precipitation and AgI–AgCl coprecipitation are $(11.35 \pm 0.17) \times 10^{-11}$ and $(1.02 \pm 0.03) \times 10^{-11}$ respectively (Table 2), which are in a good agreement with the known value of 1.138×10^{-10} and 9.954×10^{-12} , respectively. T-test of the results of $^{129}\text{I}/^{127}\text{I}$ atomic ratio at shows no significant difference between the measured value and known value at $p > 0.05$. All these features indicated that the analytical results of low level ^{129}I in the Antarctic seawater samples in this work is reliable.

A certified reference material, IAEA-418 (Mediterranean Sea water) has been analyzed using the improved coprecipitation method as well as the traditional solvent extraction method, i.e., after addition of iodine carrier and NaHSO_3 , the pH of solution was adjusted to 1-2 using HNO_3 and then after the procedures of extraction and back-extraction iodine was precipitated as AgI and finally measured by AMS. The concentrations of ^{129}I and $^{129}\text{I}/^{127}\text{I}$ atomic ratios of IAEA-418 obtained by the two method are presented in Table 2, which shows very good agreement between the

analytical results obtained by the coprecipitation method and those obtained by the solvent extraction method and shows no significant difference ($p>0.05$ for t-Test). It is confirmed that this improved method presented here is reliable. The analytical results of ^{129}I concentration in IAEA-418 seawater $((2.54\pm0.042) \times 10^8 \text{ atoms L}^{-1}$ for coprecipitation method) are agreed well with the certified value $((2.16\text{-}2.73)\times 10^8 \text{ atoms L}^{-1})$ [14].

Table 3 Comparison of Analytical Results for ^{129}I Species in Seawater from Yellow Sea by Coprecipitation (Method-1) and Ion-Exchange Chromatography (Method-2)

Species	Method	$^{129}\text{I}, \times 10^7 \text{ atom/L}$	$^{129}\text{I}/^{127}\text{I}, \times 10^{-10}$
Total iodine	Method-1	5.43 \pm 0.10	3.29 \pm 0.06
		5.47 \pm 0.11	3.31 \pm 0.07
	Method-2	5.69 \pm 0.14	3.44 \pm 0.09
		5.64 \pm 0.14	3.41 \pm 0.09
I^-	Method-1	3.93 \pm 0.07	12.99 \pm 0.22
		3.73 \pm 0.07	12.34 \pm 0.22
	Method-2	3.92 \pm 0.12	12.96 \pm 0.41
		3.99 \pm 0.11	13.2 \pm 0.38
IO_3^-	Method-1	2.14 \pm 0.07	1.59 \pm 0.05
		2.13 \pm 0.06	1.60 \pm 0.04
	Method-2	1.79 \pm 0.08	1.32 \pm 0.06
		1.92 \pm 0.08	1.42 \pm 0.06

Due to lack of certified reference materials of seawater for ^{129}I species, the improved coprecipitation method was validated by analysis of seawater sample collected from Yellow Sea by both the improved coprecipitation method presented in

this work and the conventional anion-exchange chromatography method [2, 15]. ^{129}I in the iodide, iodate, and total iodine forms separated by two methods as AgI-AgCl or AgI were measured by AMS. The concentrations and ratios of total ^{129}I , $^{129}\text{I}^-$, $^{129}\text{IO}_3^-$ obtained by the two methods are presented in Table 3, which show excellent agreement between the analytical results for ^{129}I species obtained by the coprecipitation method and those obtained by the conventional anion-exchange chromatographic method and shows no significant difference ($p>0.05$ for t-Test). This confirms that the improved coprecipitation method for speciation analysis of ^{129}I presented here is reliable and suitable for analysis of ^{129}I in seawater. In addition, the sample was analyzed twice (Table 2), and the results of these samples show a good replicability for both concentrations and ratios of ^{129}I species (RSD<5%). Meanwhile, more than 95% of iodide by using the improved coprecipitation method can be separated from seawater and cross contamination of iodine species can be ignored.

Compared with the anion-exchange chromatography method for separation of iodine species in seawater [15], the main advantages of the improved method presented in this work are less chemicals consuming, very easy to operate and separate iodine from seawater, which make this method suitable for in situ separation of iodine species on board sampling vessels during expedition. In particular, this is very suitable for the separation of low level ^{129}I from seawater collected in the area far away from nuclear activity such as the Antarctic.

Distribution of ^{129}I and ^{127}I species in seawater in the Antarctic

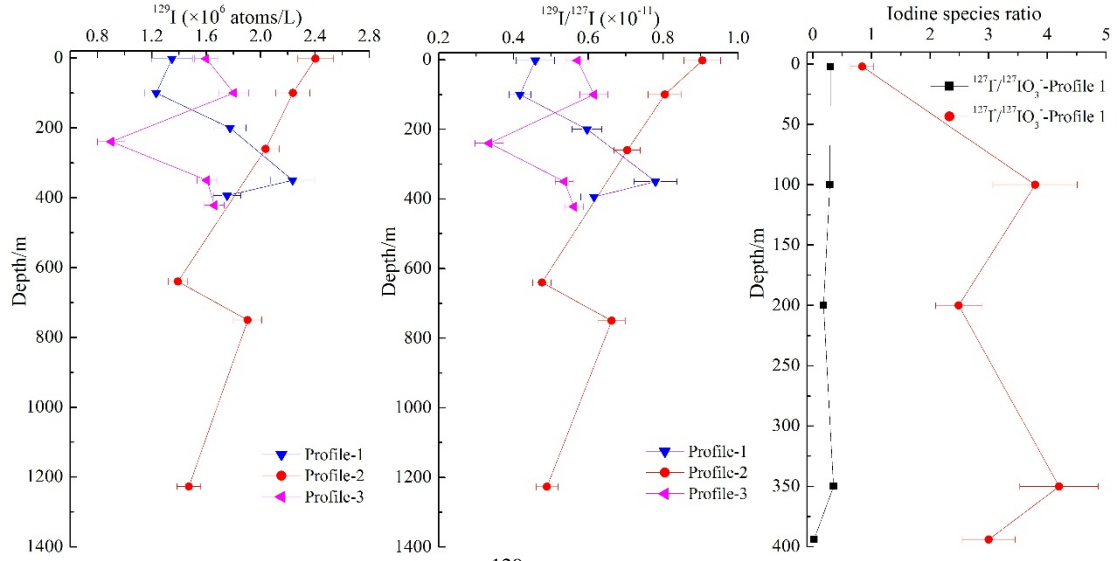


Fig. 6 Depth distribution of ^{129}I profiles, error bars showing analytical concentration (a), $^{129}\text{I}/^{127}\text{I}$ (b) and iodine species molar ratio (c) in seawater

The depth distribution of ^{129}I concentrations, $^{129}\text{I}/^{127}\text{I}$ atomic ratios and iodine species molar ratios in three Antarctic seawater profiles are presented in Fig. 6. The concentrations of ^{129}I range from 1.09×10^6 atoms/L to 2.40×10^6 atoms/L, with an average of 1.71×10^6 atoms/L, which is lower than that in the Northern Hemisphere ($>1.0 \times 10^7$ atoms/L) [16], and $^{129}\text{I}/^{127}\text{I}$ atomic ratios range from 3.7×10^{-12} to 9.0×10^{-12} , with an average of 6.0×10^{-12} , which is only 4 times higher than the pre-nuclear level (1.5×10^{-12}) in the marine system [17-20], indicating that a predominantly anthropogenic source of ^{129}I has not only reached into the Antarctic surface marine environment [21] but into the deep water down to 1227 meters. The main source of ^{129}I in the investigated area might be attributed to the global fallout of atmospheric nuclear weapons testing [21].

The vertical variations for the concentrations of ^{129}I and $^{129}\text{I}/^{127}\text{I}$ atomic ratios in the profile 2 shows a small but visible decreased trend with increase of the depth and might reflect weak vertical migration in the ice shelf zone. However, the characteristic

of vertical variation of profile 1 and 3 in the Amundsen Sea Polynya fluctuates smoothly with increase of the depth in some ranges, indicating strong vertical exchange/mixture of the water masses between the surface and the deep sea. The trend of profile 2 is similar with that in the Gulf of Mexico and the Makarov Basin, Arctic Ocean, which decreases with the increase of depth and the highest ^{129}I concentration lies near the surface (<100m) [22, 23]. The trend of profile 1 and 3 is different from that in the profile 2 and in most of the global oceans, where exponentially decreases with the increase of depth in the offshore Fukushima [24] and where the highest concentration for Beaufort Sea in the Arctic Ocean and for Toyama Bay in the Japan sea lies near the subsurface layer (~200m) and then exponentially decreases with the increase of depth [25, 26], indicating strong mixture of the water masses between the surface and subsurface layer.

The analytical results of the iodine species ratio for ^{127}I and ^{129}I show a obviously different distribution of ^{129}I compared with ^{127}I in the profile 1 (Fig. 6). The $^{127}\text{I}^-/^{127}\text{IO}_3^-$ values are normally below 0.35 and show a fairly small variation while the ratios for $^{129}\text{I}^-/^{129}\text{IO}_3^-$ lie at 0.84-4.20, indicating iodine-129 exists predominantly as iodide. This discrepancy between the iodine species ratio for ^{127}I and ^{129}I likely reflects different sources of the isotopes and comparatively long time to reach equilibrium between iodide and iodate in the open sea. It is well known that iodine mainly exists as iodate in the open sea and as iodide in the coastal water and surface water by reduction of iodate through some procedures, such as biological activity, photochemical and chemical reactions [2, 24]. Profile 1 was collected from an open sea, and the $^{127}\text{I}^-/^{127}\text{IO}_3^-$ ratios are typical values for the open sea. Meanwhile, there are higher concentrations of phosphate, nitrite, total nitrogen, silicate, pCO_2 and lower concentrations of chlorophyll, ammonium in the whole profile (Table 1), indicating the relatively weak biological activity. Therefore, the ^{129}I species should stem from its source. However, the higher

$^{129}\text{I}/^{129}\text{IO}_3^-$ values in the deep sea might reflect strong vertical mixture of water masses and originate from the upwelling of circumpolar deep water [27] that carried the higher $^{129}\text{I}/^{129}\text{IO}_3^-$ values. These results indicate that the chemical speciation analysis of ^{129}I can be used to investigate the transport, dispersion, and mixture of the water masses. This work is a preliminary result of the investigation for the dispersion and mixing of water in the Antarctic, a further investigation is in preparation.

Acknowledgements

Financial supports from the Ministry of Science and Technology of China (2015FY110800), as well as State Key Laboratory of Loess and Quaternary Geology are gratefully acknowledged.

References

1. Wong GTF (1991) The Marine Geochemistry of iodine. *Reviews in Aquatic Sciences* 4:45-73
2. Hou XL, Aldahan A, Nielsen SP, Possnert G, Nies H, Hedfors J (2007) Speciation of ^{129}I and ^{127}I in seawater and implications for sources and transport pathways in the North Sea. *Environ Sci Technol* 41:5993-5999
3. Hou XL, Hansen V, Aldahan A, Possnert G, Lind OC, Lujanienė G (2009) A review on speciation of iodine-129 in the environmental and biological samples. *Anal Chim Acta* 632:181-196
4. Nishiizumi K, Elmore D, Honda M, Arnold JR, Gove HE (1983) Measurements of ^{129}I in meteorites and lunar rock by tandem accelerator mass spectrometry. *Nature* 305:611-612
5. Rao U, Fehn U (1999) Sources and reservoirs of anthropogenic iodine-129 in western New York. *Geochim Cosmochim Acta* 63:1927-1938
6. Luo MY, Hou XL, He CH, Liu Q, Fan YK (2013) Speciation analysis of ^{129}I in seawater by carrier-free AgI-AgCl coprecipitation and accelerator mass spectrometric measurement. *Anal Chim* 85:3715-3722

7. Fehn U, Snyder G, Egeberg PK (2000) Dating of pore waters with ^{129}I : relevance for the origin of marine gas hydrates. *Science* 289:2332-2335
8. Keogh SM, Aldahan A, Possnert G, Finegan P, Vintro LL, Mitchell PI (2007) Trends in the spatial and temporal distribution of ^{129}I and ^{99}Tc in coastal waters surrounding Ireland using *Fucus vesiculosus* as a bio-indicator. *J Environ Radioact* 95:23-38
9. Raisbeck GM, Yiou F (1999) ^{129}I in the oceans: origins and applications. *Sci Total Environ* 237–238:31-41
10. Reithmeier H, Lazarev V, Rühm W, Schwikowski TM, Gäggeler HW, Nolte E (2006) Estimate of European ^{129}I releases supported by ^{129}I analysis in an Alpine ice core. *Environ Sci Technol* 40: 5891-5896
11. Santschi PH, Schwehr KA (2004) $^{129}\text{I}/^{127}\text{I}$ as a new environmental tracer or geochronometer for biogeochemical or hydrodynamic processes in the hydrosphere and geosphere: the central role of organo-iodine. *Sci Total Environ* 321:257-271
12. Hou XL, Zhou WJ, Chen N, Zhang LY, Liu Q, Luo MY, Fan YK, Liang W, G., Fu YC (2010) Determination of Ultralow Level $^{129}\text{I}/^{127}\text{I}$ in Natural Samples by Separation of Microgram Carrier Free Iodine and Accelerator Mass Spectrometry Detection. *Anal Chim* 82:7713-7721
13. Zhou W, Hou X, Chen N (2010) Preliminary study of radioisotope ^{129}I application in china using Xi'an accelerator mass spectrometer. *INCS News* 25:8-23
14. M. K. Pham, M. Betti, P. P. Povinec, V. Alfimov, D. Biddulph, J. Gastaud, W. E. Kieser, J. M. Lo'pez Gutie'rrez, G. Possnert, J. A. Sanchez-Cabeza *et al* (2010) Certified reference material IAEA-418: ^{129}I in Mediterranean Sea water. *J Radioanal Nucl Chem* 286:121-127
15. Hou XL, Dahlgaard H, Nielsen SP (2001) Chemical speciation analysis of ^{129}I in seawater and a preliminary investigation to use it as a tracer for geochemical cycle study of stable iodine. *Mar Chem* 74:145-155
16. Snyder G, Aldahan A, Possnert G (2010) Global distribution and long-term fate of anthropogenic ^{129}I in marine and surface water reservoirs. *Geochem Geophys Geosyst* 11:1-19
17. Fehn U, Moran JE, Snyder GT, Muramatsu Y (2007) The initial $^{129}\text{I}/\text{I}$ ratio and the presence of 'old' iodine in continental margins. *Nucl Instrum Methods Phys Res Sect B* 259:496-502

18. Fehn U, Snyder G (2000) ^{129}I in the Southern Hemisphere: Global redistribution of an anthropogenic isotope. *Nucl Instrum Methods Phys Res Sect B* 172:366-371
19. Moran JE, Fehn U, Hanor JS (1995) Determination of source ages and migration patterns of brines from the U.S. Gulf Coast basin using ^{129}I . *Geochim Cosmochim Acta* 59:5055-5069
20. Moran JE, Fehn U, Teng RTD (1998) Variations in $^{129}\text{I}/^{127}\text{I}$ ratios in recent marine sediments: evidence for a fossil organic component. *Chem Geol* 152:193-203
21. Xing S, Hou XL, Aldahan A, Possnert G, Shi KL, Yi P, Zhou WJ (2015) Iodine-129 in Snow and Seawater in the Antarctic: Level and Source. *Environ Sci Technol* 49:6691-6700
22. Alfimov V, Aldahan A, Possnert G, Winsor P (2004) Anthropogenic iodine-129 in seawater along a transect from the Norwegian coastal current to the North Pole. *Mar Pollut Bull* 49:1097-1104
23. Schink DR, Santschi PH, Corapcioglu O, Sharma P, Fehn U (1995) ^{129}I in Gulf of Mexico waters. *Earth Planet Sci Lett* 135:131-138
24. Hou XL, Povinec PP, Zhang LY, Shi KL, Biddulph D, Chang C-C, Fan YK, Golser R, Hou YK, Jeřkovský M *et al* (2013) Iodine-129 in seawater offshore Fukushima: distribution, inorganic speciation, sources, and budget. *Environ Sci Technol* 47:3091-3098
25. Smith JN, Ellis KM, Kilius LR (1998) ^{129}I and ^{137}Cs tracer measurements in the Arctic Ocean. *Deep Sea Res I* 45:959-984
26. Suzuki T, Kabuto S, Amano H, Togawa O (2008) Measurement of iodine-129 in seawater samples collected from the Japan Sea area using accelerator mass spectrometry: Contribution of nuclear fuel reprocessing plants. *Quat Geochronol* 3:268-275
27. Yabuki T, Suga T, Hanawa K, Matsuoka K, Kiwada H, Watanabe T (2006) Possible source of the antarctic bottom water in the Prydz Bay Region. *J of Oceanogr* 62:649-655